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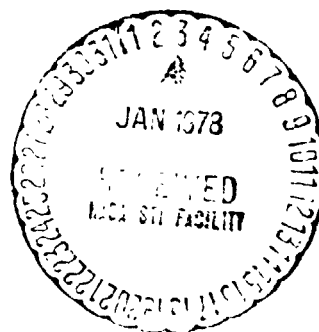
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**VOLATILE PRODUCTS FROM THE INTERACTION OF KCl(g) WITH
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VOLATILE PRODUCTS FROM THE INTERACTION OF KCl(g) WITH Cr_2O_3 AND LaCrO_3 IN OXIDIZING ENVIRONMENTS

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ABSTRACT

Cooled target collection techniques and high pressure mass spectrometric sampling were used to measure the relative rates of oxidative vaporization and to identify the volatile products emanating from samples of chromia (Cr_2O_3) and Mg-doped lanthanum chromite ($\text{LaMg}_{0.21}\text{Cr}_{1.35}\text{O}_{3.4}$). The materials were exposed to partial pressures of KCl(g) with and without $\text{H}_2\text{O(g)}$ in one atmosphere of slowly flowing oxygen at elevated temperatures. Chromia and fresh samples of lanthanum chromite exhibited enhanced rates of oxidative vaporization upon exposure to these reactants. Mass spectrometric identification showed that the enhancements resulted from the heterogeneous formation of complex molecules of the type $(\text{KCl})_{1,2,3}\text{CrO}_3$ and $(\text{KOH})_{1,2}\text{CrO}_3$. Lanthanum chromite that had undergone prolonged oxidative vaporization exhibited no enhanced oxidation upon exposure to the reactants.

INTRODUCTION

Equilibrium thermodynamic calculations applied to gas turbine engines operating under conditions conducive to hot corrosion attack indicate that the engine hot section environment should be relatively rich in the contaminant gases NaCl(g) , NaOH(g) , and HCl(g) (ref. 1). Similarly, coal-fired systems are also expected to contain the additional species KCl(g) and KOH(g) . The role that such gaseous species play in high temperature corrosion is not well characterized. We have been investigating the interaction of such reactant gases with metals and metal oxides at elevated temperatures in oxidizing

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environments at atmospheric pressure. Our experimental studies employ two different techniques: (1) cooled target collection to determine relative rates of oxidative vaporization of samples exposed to various oxidizing environments; (2) high pressure molecular beam mass spectrometric sampling to identify molecules volatilizing from the samples.

Recently, we reported results obtained for the systems Cr, Mo, Ti, and four superalloys exposed to oxygen containing water and gaseous NaCl (refs. 2 and 3). We showed that volatile products were detected for all these materials except alloy B-1900 and titanium, and that the rates of oxidative vaporization were markedly enhanced by $H_2O(g)$, $NaCl(g)$, and $H_2O(g) + NaCl(g)$. We further showed that the complex molecules effecting the increased rates of oxidative vaporization in the systems containing chromium were of the types: $(NaCl)_xCrO_3$ where $x=1, 2$, and 3 ; $(NaOH)_xCrO_3$ where $x=1$ and 2 ; $Na_2Cr_2O_7$; and, $^xCrO_2(OH)_2$. For the systems containing molybdenum the types were similar; namely, $(NaCl)_x(MoO_3)_3$ where $x=1$ and 2 , $NaOH(MoO_3)_3$, and $MoO_2(OH)_2$.

The work reported herein extends these investigations to systems involving the interaction of $KCl(g)$ with oxidized chromium and lanthanum chromite; that is, $Cr + O_2 \pm KCl(g) \pm H_2O(g)$ and $LaCrO_3 + O_2 \pm KCl(g) \pm H_2O(g)$.

EXPERIMENTAL

Experimental Procedures. - Two experimental techniques were used in the present atmospheric pressure investigations: cooled target collection and high pressure mass spectrometric sampling. A schematic of each apparatus is shown in figure 1. It can be seen that the furnace assembly was common to both techniques. Two different furnaces were employed in this study: a low temperature furnace operated in the range 850° to $1100^\circ C$, and an high temperature furnace operated between 1000° and $1500^\circ C$. The former is depicted in figure 1. It was 15 cm long and was operated with a 2.2 cm i.d. quartz sample-containment tube. The high temperature furnace was platinum wound and was 20 cm long. It was operated with a 2.2 cm i.d. high purity alumina containment tube. The oxidation samples (approx. $1 \times 2 \times 0.25$ cm) were suspended in the containment tubes by a Pt 13% Rh wire. The furnace temperature was controlled through a thermocouple by a precision set-point current proportionating controller coupled to a saturable core reactor power source. Temperatures could be maintained to $\pm 2^\circ C$. Sample temperature was measured independently with a Pt-Pt 13% Rh thermocouple inside the containment tube and contacting the side of the sample.

Partial pressures of $KCl(g)$ were developed by heating $KCl(c)$ in a platinum crucible that was situated below the sample in a 1.3 cm diameter quartz tube (alumina in the high temperature furnace). The crucible was 2 cm long by 0.6 cm in diameter and it was supported on a

double bore alumina thermocouple tube. A Pt-Pt 13% Rh thermocouple in the alumina tube extended into the crucible base and facilitated continuous measurement of the crucible temperature. A slip-seal system allowed the crucible assembly to be moved vertically so that the crucible temperature could be varied by changing its position in the furnace. The crucible temperature was maintained considerably lower than the sample temperature to insure no condensation of KCl on the sample.

Metered oxygen flows were supplied independently to both concentric tubes. Flows were adjusted to gas velocities of 0.7 and 2.5 cm sec⁻¹ for the outer and inner tubes respectively. The oxygen supplied to the outer tube could be saturated with water vapor at room temperature by passing the gas through a fritted glass plug in the bottom of a 20 cm high column of water. The mass fraction of KCl(g) in the apparatus was determined from the weight loss (per unit time) of KCl(c) in the crucible and the volume flow rate of gas through the apparatus. No attempt was made to apply corrections to the KCl(g) concentrations for collision and reactions with the wall of the apparatus. In the target collection experiments a mass fraction of about 20 ppm KCl(g) was used, and in the mass spectrometric sampling experiments KCl(g) concentrations of 700 ppm were generally employed.

In target collection experiments, figure 1 (a), samples were usually preoxidized for several hours at high temperature. Experiments were started by adding reactant gases and five minutes were allowed to elapse before collection was begun. The volatile products coming from the sample were collected on polished platinum targets (5x5x0.04cm) attached to a water-cooled copper plate. The target was positioned 1cm above the end of the furnace in the low temperature furnace and 2.5cm in the high temperature furnace. A platinum collimator with a 2cm diameter opening was located between the target and the furnace. Deposits collected in measured times were dissolved in water, and the resulting solutions analyzed for metal cations by atomic absorption spectroscopy. Experiments run in oxygen alone and in the high temperature furnace resulted in deposits that were insoluble in water and acids. Apparently, the CrO₃ deposit was decomposing to Cr₂O₃. These deposits were dissolved by fusing in K₂S₂O₈. In all experiments using LaCrO₃ samples, deposits were also treated with 1:1 HCl to dissolve any lanthanum oxides that might have been collected.

Identification of volatile species emanating from samples was accomplished with the high pressure mass spectrometric sampler positioned at the containment tube opening as shown in figure 1(b). The high pressure, free-jet expansion, modulated molecular beam, mass spectrometric sampler facilitates direct mass spectrometric analysis of atmospheric pressure sources. This technique preserves the dynamic and chemical integrity of sampled species. The theory and details of the free-jet expansion sampling technique are given in reference 4

which also includes a detailed description of our instrument.

For our sampler the inlet orifice was 0.022 cm in diameter, located at the apex of a 106 degree included angle cone fabricated from 0.025 cm thick Pt 10% Rh. The cone was welded on the end of a 1.5 cm long by 2.0 cm diameter stainless steel tube. The sampling cone protruded into the quartz tube about 1 cm and was heated to a temperature approaching that of the sample. Heating of the orifice was necessary to minimize condensation on and subsequent clogging of the orifice by KCl and other condensable gas species.

Materials.- The chromium used in this study was iodide chromium of 99.99+% purity. Typical analysis showed a total metallic impurity of 15 ppm. Samples were cut with a diamond saw and used, without surface preparation, after degreasing.

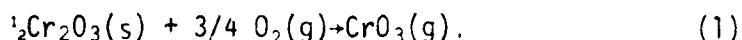
The lanthanum chromite used was Westinghouse lanthanum chromite* that was formed by hot pressing. The nominal composition was $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$. Chemical analysis* indicated that the material contained excess chromium and magnesium as described by the formula $\text{LaMg}_{0.21}\text{Cr}_{1.35}\text{O}_{3.4}$ or $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3 \cdot \text{Mg}_{0.16}\text{Cr}_{0.4}\text{O}_{0.4}$. Light micrographs of polished cross sections of the material revealed micrometer-sized occlusions of a second phase. Electron probe microanalysis of these occlusions indicated they contained larger amounts of chromium and magnesium, compared to the matrix. They also behaved as a sink for the impurities. Samples were cut with a diamond saw and degreased with trichloroethane, acetone, and alcohol.

RESULTS AND DISCUSSION

Cr_2O_3 STUDIES

Target collection experiments. - The effects of exposing hot oxidizing chromium to partial pressures of $\text{H}_2\text{O}(\text{g})$, $\text{KCl}(\text{g})$ and $\text{KCl}(\text{a}) + \text{H}_2\text{O}(\text{g})$ were studied. The rate of collection of chromium, volatilizing from the sample as gaseous compounds, was determined for the temperature range 900° to 1100°C. New samples were preoxidized four hours or longer before rate measurements were made.

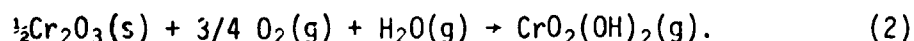
Results are presented in figure 2 in an Arrhenius plot. The triangular set of points are the rates determined for simple oxidative vaporization, in slowly flowing oxygen at one atmosphere pressure, represented by the reaction:



*We are indebted to Barry R. Rossing of the Westinghouse Electric Corporation for kindly supplying us with samples of this material and with chemical analyses of same.

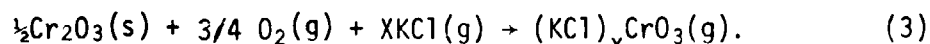
The line drawn through the points was obtained by a least-squares analysis of the data and the slope of this line yields an energy of activation, E_a , of 48.4 kcal mole⁻¹. This value is somewhat less than that reported by Stearns, Kohl, and Fryburg (ref. 5) for experimental conditions in which the rate was "reaction controlled." The lower value found here indicates that "diffusion control" conditions are influencing the measured rate (ref. 6). This condition is not critical to results reported herein because we are primarily interested in relative values.

The circular points (fig. 2) represent the rates found when water vapor (20 torr) was added to the oxygen; i.e., for the reaction



We have assumed that reactions (1) and (2) occur independently, and the circular points have been corrected by subtracting the contribution from simple oxidative vaporization. The volatilizing hydrate, $\text{CrO}_2(\text{OH})_2(\text{g})$, was identified in our previous mass spectrometric studies of this reaction (ref. 3). The least-squares line determined for the data points yields an activation energy of 33.0 kcal mole⁻¹, slightly lower than that found for simple oxidative vaporization.

The square points represent the rates found when $\text{KCl}(\text{g})$ (20 ppm) was added to the oxygen; i.e., for reaction:



The rates have been corrected for simple oxidative vaporization; the volatilizing molecules, $(\text{KCl})_x\text{CrO}_3(\text{g})$, are the main species found in our mass spectrometric studies which will be discussed in the next section. It should be noted that addition of $\text{KCl}(\text{g})$ to the oxygen results in a marked enhancement in the rate of oxidative vaporization of chromium. The results also show that the formation of these complex $(\text{KCl})_x\text{CrO}_3(\text{g})$ molecules requires little energy of activation: the slope of the least-squares line through the square points gives an activation energy of 2.5 kcal mole⁻¹.

The rates found when both $\text{H}_2\text{O}(\text{g})$ and $\text{KCl}(\text{g})$ were added to the oxygen are represented by the diamond points. The rates have been corrected for simple oxidative vaporization. The results indicate that a further marked enhancement in the rate has occurred; in fact, the rates are considerably greater than the sum of reactions (2) and (3). These data were not fitted to a straight line, and no activation energy was determined, because these rates represent the sum of several reactions and the data are not expected to lie on a straight line. The dashed line is merely a smooth curve drawn through the points. These rates are seen to be fairly independent of temperature, but with an upward curvature around 1100°C. This probably results from the contribution of reaction (2).

It should be noted that the marked enhancements found in the rates of oxidative vaporization of chromium upon the addition of $\text{H}_2\text{O}(\text{g})$, $\text{KCl}(\text{g})$, and $\text{H}_2\text{O}(\text{g}) + \text{KCl}(\text{g})$ to oxygen precludes a gas-phase reaction explanation of the formation of the complex volatile chromium species. If the volatile species were formed in the gas-phase by reaction with $\text{CrO}_3(\text{g})$, the rates would be limited by the rate of formation of $\text{CrO}_3(\text{g})$ and no enhancements would be observed.

The dependence of the rate on oxygen pressure and on $\text{KCl}(\text{g})$ pressure was studied for reaction (3). The rate for one of our samples (in $\mu\text{g hr}^{-1}$) versus the O_2 pressure is presented in figure 3 for a chromium temperature of 935°C and a $\text{KCl}(\text{g})$ partial pressure of 20 ppm. The O_2 partial pressure was varied by dilution with argon, and the total pressure was maintained at 750 torr. The points have not been corrected for simple oxidative vaporization, but this would on the average amount to only a 3% correction. The points fall fairly close to the straight line indicating a first-order dependence on O_2 pressure.

The rate for this same sample in $\mu\text{g hr}^{-1}$ versus the "effective pressure" of KCl is presented in figure 4 in log-log format. The chromium temperature was constant at 935°C and the O_2 pressure was 750 torr. The "effective pressure" of $\text{KCl}(\text{g})$ was defined as:

$$P_{\text{KCl}} (\text{effective}) = P_{\text{KCl}} + 2 P_{\text{K}_2\text{Cl}_2} \quad (4)$$

where P_{KCl} and $P_{\text{K}_2\text{Cl}_2}$ are the vapor pressures of the monomer and dimer, respectively. This "effective pressure" is not the absolute pressure of KCl in the apparatus, but it is proportional to the number of moles of KCl available for reaction at the chromium surface. The "effective pressure" was varied by changing the temperature of the KCl crucible from 570° to 780°C in these experiments. The slope of the least-squares line drawn through the points was 0.94 indicating that the reaction was also first order with respect to KCl .

These dependencies on partial pressure of oxygen and "effective" pressure of KCl found for reaction (3) are similar to those found for the analogous reaction with $\text{NaCl}(\text{g})$ (ref. 2).

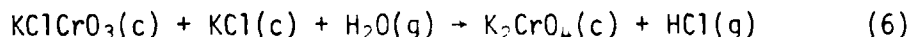
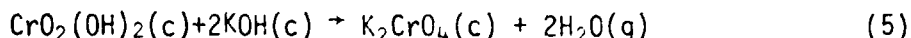
Mass spectrometric experiments. - High pressure modulated molecular beam mass spectrometric sampling was used to identify and to measure the volatile species emanating from the hot oxidizing chromium samples exposed to partial pressures of $\text{KCl}(\text{g})$ with and without $\text{H}_2\text{O}(\text{g})$. The main ions identified are presented in figure 5 together with their measured relative intensities and probable parent molecule. The ions were identified by their m/e values, isotropic distribution, and behavior when either $\text{KCl}(\text{g})$, $\text{H}_2\text{O}(\text{g})$ or the sample were removed from the system. The reported relative intensities can be converted to correct ratio of partial pressures only if reliable values are available for the relative ionization and fragmentation cross sections, multiplier gains for each ion, quadrupole mass filter trans-

mission as a function of m/e , and Mach-number focusing factors for each species. At present, most of these quantities are unknown for the complex molecular species presented in the tables. Finally, parent molecular species were assigned on the basis of familiarity with the mass spectrum-molecular composition relationships for other inorganic halide molecule systems. It is well established (ref. 7) that halogen-containing molecules fragment upon electron impact ionization to yield molecular ions with the loss of a halogen atom.

The ion intensities given in figure 5 have been normalized with respect to a value of unity for the O_2^+ peak at one atmosphere of oxygen. In addition to the ions resulting from the KCl, a number of ions containing chromium were observed. A small amount of CrO_3 , which arises from the oxidative vaporization of Cr_2O_3 , was observed. But mainly, chromium occurred in complexes of KCl and CrO_3 with the general formula $(KCl)_xCrO_3$ where $x=1,2$, and 3, $(KCl)_2CrO_3$ being the most prominent species. Similar complexes of KOH and CrO_3 were discovered with the formula $(KOH)_xCrO_3$ where $x=1$ or 2. The KOH originates from the hydrolysis of the KCl.³ This fact accounts for the effects observed when water content of the oxygen was increased; namely, (1) a slight decrease in KCl and its polymers; (2) a large increase in the KOH complexes, and (3) a very large increase in KOH. The fact that KOH-containing species were observed when no water was added indicates that the system was not completely free of water vapor. No special precautions were taken to dry the oxygen or the KCl used in these experiments, so the result is not surprising.

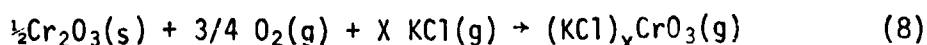
We often observed deposits of yellow needles around the top of the furnaces. An X-ray diffraction analysis revealed that these needles were K_2CrO_4 . We were unable to detect any ions in our mass spectrometer that corresponded to K_2CrO_4 .

The origin of the K_2CrO_4 needles probably depends on heterogeneous reactions of the following type:

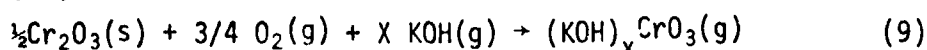


However, we did observe ions ascribable to $K_2Cr_2O_7$ and complex molecules of the dichromate with KCl and/or KOH.

These results with the $Cr_2O_3(s) + O_2 + KCl(g) + H_2O(g)$ system are very similar to the results we have obtained with the $Cr_2O_3(s) + O_2 + NaCl(g) + H_2O(g)$ system (ref. 3). For comparison, we have reproduced the NaCl results in figure 6 using the format of figure 5. As with the NaCl system, the main reactions responsible for the transport of chromium in the KCl system are:



where $x=1, 2$, and 3 ; and

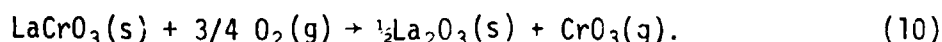


where $x=1$ and 2 .

As stated previously, the enhanced rates of oxidation obtained in the target collection studies in the presence of $\text{KCl}(\text{g})$ and $\text{KOH}(\text{g})$ preclude a gas phase reaction explanation of the formation of these complex molecules. A gas-phase mechanism would be limited by the rate of formation of $\text{CrO}_3(\text{g})$.

LaCrO₃ STUDIES

Target collection experiments. - Simple oxidative vaporization of LaCrO_3 was studied in the temperature range 1050° to 1520°C :



For comparison, the oxidative vaporization of oxidized chromium, reaction (1), was also studied in the same temperature range. The results are presented in figure 7 in an Arrhenius plot, and the lines drawn are from a least-squares analysis of the data points. Comparison of these rates for oxidized chromium with those obtained in the lower temperature furnace for the temperature range 900° to 1100°C (fig. 2) reveals that the rates are roughly one-half as large. This probably resulted from the larger sample-to-target distance necessitated by the higher temperatures of the furnace. Different uncontrollable aerodynamic flow conditions may also contribute, as indicated by the difference in the energies of activation determined in the two temperature regimes: $E_a = 48.8 \text{ kcal mole}^{-1}$ for low temperature furnace data; and $E_a = 53.6 \text{ kcal mole}^{-1}$ for high temperature furnace data. These discrepancies emphasize the relative nature of the numerical results.

Comparison of the oxidized chromium rates with the LaCrO_3 rates (fig. 7) shows that oxidative vaporization from LaCrO_3 occurs much more slowly, and with a higher energy of activation; namely, $72.1 \text{ kcal mole}^{-1}$. Prior to obtaining these LaCrO_3 results, the sample was preoxidized for 20 hours at 1300°C . The results were obtained randomly with respect to temperature and seemed unaffected by the La_2O_3 that builds up on the surface during oxidative vaporization (reaction (10)). This result is similar to that obtained by Chatterji et al. (ref. 8). In situ X-ray diffraction analysis of samples after oxidation indicated the presence of La_2O_3 and $\text{La}(\text{OH})_3$ on the surface. The oxide was usually the more prominent and the hydroxide was probably formed from it by hydrolysis with the water vapor in the air.

Exposure of a LaCrO_3 sample that had undergone prolonged oxidation to oxygen containing KCl(g) and $\text{KCl(g)} + \text{H}_2\text{O(g)}$, resulted in no enhancement in the rate of oxidative vaporization. However, if a fresh sample (one that had undergone no preoxidation) was exposed, large enhancements were observed. This is shown in figure 7 where the square points represent a series of rates measured in $\text{O}_2 + \text{KCl(g)} + \text{H}_2\text{O(g)}$ at 1250°C , and the diamond points represent a series measured in $\text{O}_2 + \text{KCl(g)}$ at 1300°C . Usually, rates were determined for one hour periods except when the sample was run overnight or, in some cases, removed from the furnace until morning. It required around 30 to 40 hours of total running time for the disappearance of the enhancement in the rates. For comparison, the behavior of a fresh sample in straight oxidation at 1340°C is depicted by the solid circular points. Here also, an enhancement was observed in the rates until 30 hours of total oxidation time had been completed.

These enhanced rates observed with fresh samples probably result from the large excess of chromium in these samples, especially from the surface occlusions. Similar behavior was observed by Chatterji et al. (ref. 8). Apparently, the excess chromium was removed from the effective reaction zone in periods of about 30 hours.

It should be noted that lanthanum was detected on the targets after long oxidation runs above 1300°C . The rate of collection was of the order of $0.3\mu\text{g cm}^{-2}\text{hr}^{-1}$ at 1340°C . This is roughly 10^{-4} of the rate of collection of chromium. No lanthanum was found in runs in which KCl(g) or $\text{KCl(g)} + \text{H}_2\text{O(g)}$ were used as reactants in the oxygen. It is surprising that lanthanum should vaporize at these relatively low temperatures: vaporization of La_2O_3 becomes measureable around 2000°C (ref. 9).

Mass spectrometric experiments. - Samples of LaCrO_3 were examined in the temperature range 1100° to 1300°C in oxygen containing $\text{KCl(g)} + \text{H}_2\text{O(g)}$. For fresh samples most of the complex molecules observed with Cr_2O_3 samples were detected, though at reduced levels. With samples that had been heated over 30 hours, no chromium-containing molecules were detectable. No lanthanum-containing molecules were observed for either type LaCrO_3 sample.

CONCLUDING REMARKS

These results have shown that KCl(g) behaves analogously to NaCl(g) upon interaction with chromium in oxidizing environments at elevated temperature. Enhanced rates of transport of chromium from the sample are effected by the heterogenous formation of volatile complex molecules of the type $(\text{KCl})_x\text{CrO}_3$ where $x=1, 2$, and 3 ; and of the type $(\text{KOH})_x\text{CrO}_3$ where $x=1$ and 2 . The proportion of the latter is dependent

on the $\text{H}_2\text{O}(\text{g})$ content of the environment.

Similar results were found for lanthanum chromite that contained a large excess of chromium. However, this rate enhancement decreased with continued exposure until it disappeared, indicating that stoichiometric lanthanum chromite would probably be inert to $\text{KCl}(\text{g})$, $\text{KOH}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ in high temperature oxidizing environments.

ACKNOWLEDGMENTS

We are indebted to J. W. Graab and W. F. Davies for performing the numerous chemical analyses required in this study.

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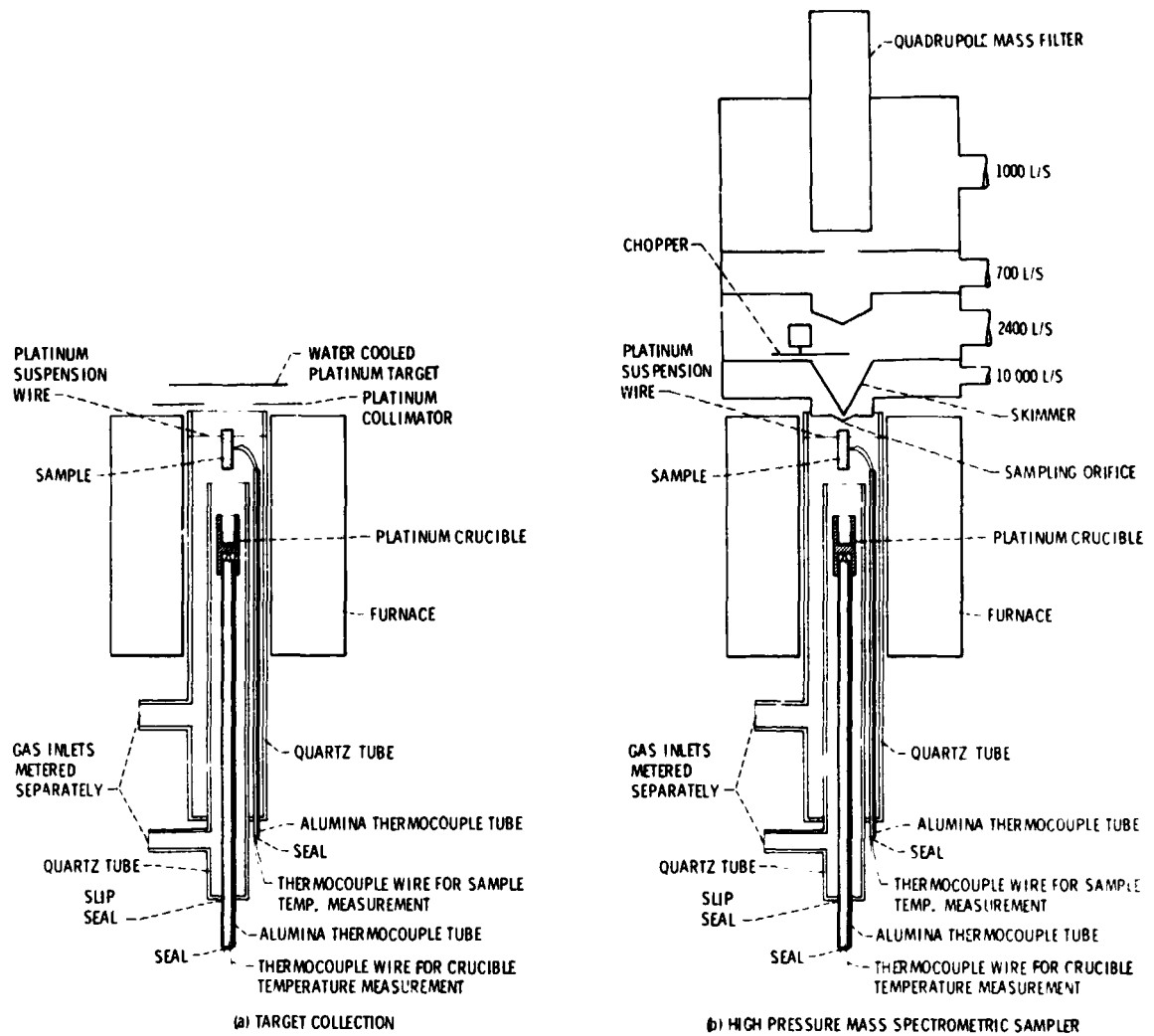


Figure 1. - Schematic of apparatus.

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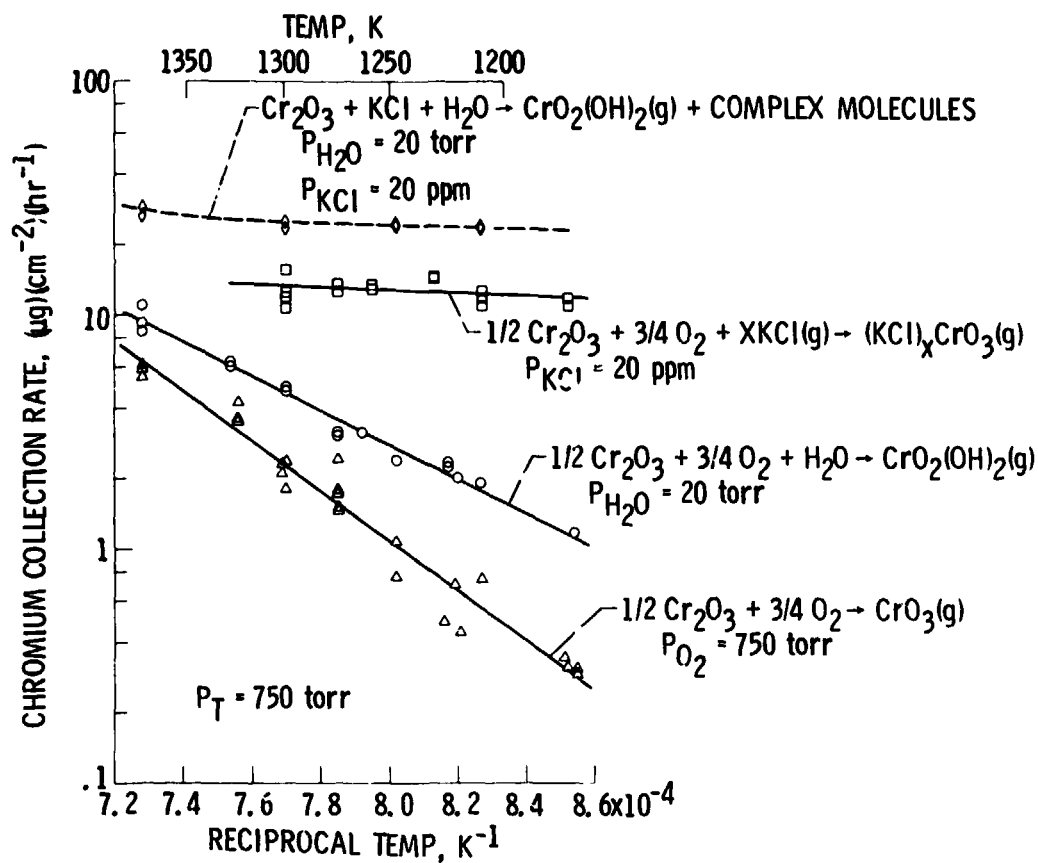


Figure 2. - Dependence of chromium collection rate on temperature of Cr_2O_3 in various reactant environments.

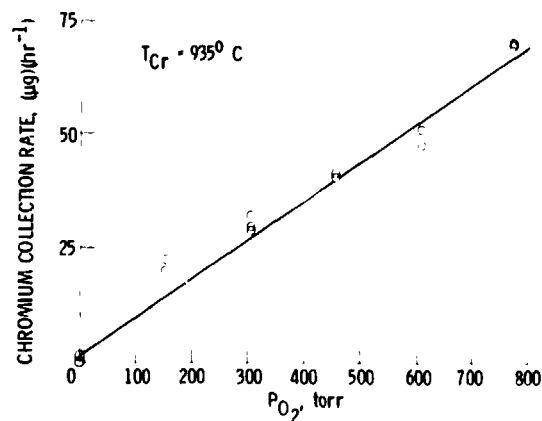


Figure 3. - Dependence of chromium collection rate from Cr_2O_3 on oxygen partial pressure in presence of 20 ppm $\text{KCl}(\text{g})$.

Figure 1 is a horizontal bar chart showing the distribution of molecular weights (M_n) for various polyacrylate copolymers. The x-axis is logarithmic, ranging from 10^{-8} to 10^{-4} . The y-axis lists 14 different copolymer compositions. For each composition, two bars are shown: a solid black bar representing the distribution 'WITH 0.1% H_2O_2 ' and an open white bar representing the distribution 'WITH 4% H_2O_2 , 20 Torr'. The legend at the bottom indicates these two conditions. The molecular weight generally decreases as the amount of H_2O_2 increases, with the most significant reduction seen for Na_2CrO_7 and $Na_2O_4C_2Cr_3$.

Copolymer Composition	Condition	Approximate M_n Range
Na^+	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$NaCl^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
Na_2Cl^+	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2Cr_2^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2Cr_2^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2Cr_2^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2CrO_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$
	WITH 4% H_2O_2 , 20 Torr	$10^{-7.5}$ to $10^{-5.5}$
$Na_2O_4C_2Cr_3^+$	WITH 0.1% H_2O_2	$10^{-7.5}$ to $10^{-5.5}$

Fig. 10 - Mass spectrum of vapors over $\text{C}_2\text{H}_5\text{I} + \text{C}_2\text{H}_5\text{Br} + \text{NaCl}$ at 4.05 G at 0.25 Torr; ion intensities relative to I^+ at $m/z = 127$.

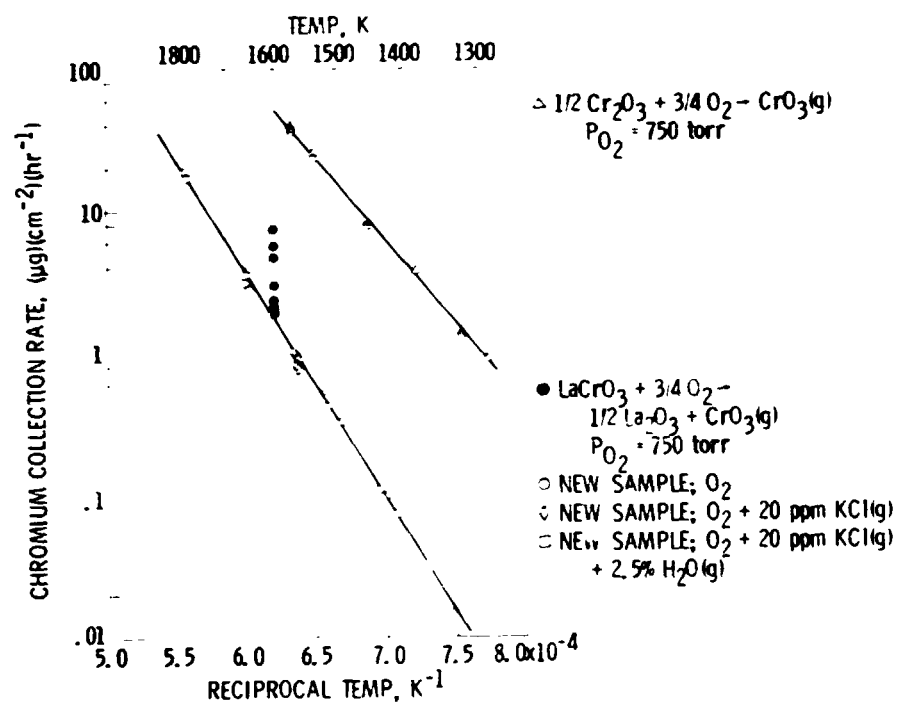


Figure 7. - Dependence of chromium collection rate on temperature of Cr_2O_3 or LaCrO_3 .

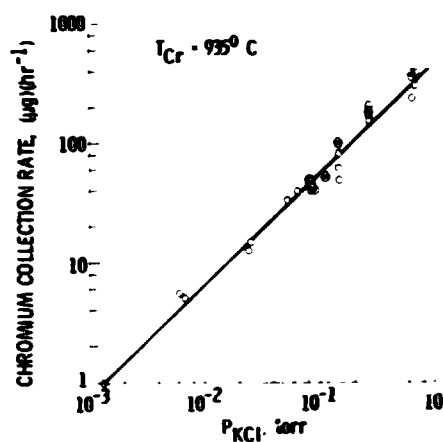
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Figure 4. - Dependence of chromium collection rate from Cr_2O_3 on effective KCl(g) partial pressure in one atmosphere of oxygen.

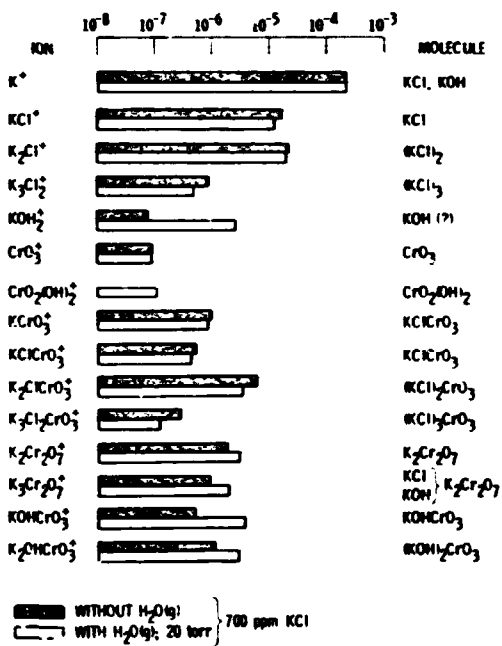


Figure 5. - Mass spectrum of vapors over $\text{Cr}_2\text{O}_3(\text{s}) + \text{O}_2(\text{g}) + \text{KCl(g)}$ $\pm \text{H}_2\text{O(g)}$ at 1204°C . Ion intensities relative to $1 \text{ atm } \text{O}_2 = 1$.